

**HYDROPHOBIC CATIONIC DISPERSIONS STABILIZED  
BY MALEIMIDE COPOLYMERS OF LOW MOLECULAR  
MASS, FOR THE SIZING OF PAPER**

The present invention relates to the field of  
5 the sizing of paper and in particular to sizing agents  
based on an aqueous cationic dispersion of hydrophobic  
polymers. It also relates to the process for producing  
such dispersions.

A good sizing agent is desired for every kind  
10 of paper, in particular printing and writing paper,  
paper for labels, wastepaper and wrapping paper.

Two kinds of sizing agents generally exist:  
surface or internal sizing agents. The term "surface  
sizing agent" is understood to mean an agent applied at  
15 the surface of papers, generally in conjunction with  
starch, using a size press; on the other hand, the term  
"internal sizing agent" is understood to mean an agent  
added with the fibres in the wet part of the  
manufacture of the paper.

20 A good surface sizing agent allows paper  
manufacturers to obtain a paper with good resistance to  
water while reducing and even sometimes eliminating  
internal sizing, which requires a larger amount of  
product than surface sizing. It also makes it possible  
25 to obtain a paper with good surface properties, which  
are particularly important in obtaining good  
printability properties on papers.

It is now known to a person skilled in the art to use, as surface sizing agent, emulsified or dispersed polymers, in combination with starch, in preference to dissolved polymers. They make it possible  
5 to obtain sizing agents having a high solids content with a low viscosity. They cause less of a foaming problem than dissolved polymers of the styrene-acrylic acid or styrene-maleic anhydride type, for example. These dispersions can be anionic or cationic, the  
10 latter being less common and more difficult to synthesize.

As far as internal sizing agents are concerned, a person skilled in the art is looking for a product which can be used without a retention agent and  
15 without a maturing stage. The commonest internal sizing agents are alkyl ketene dimer (AKD), alkyl succinic anhydrides (ASA) and colophonies. They are not suitable under all manufacturing conditions and with regard to all types of pulps and sometimes require the use of a  
20 cationic promoter.

Surface sizing agents are known to a person skilled in the art and exist in the form of anionic dispersions. They are copiously described in the literature. They are synthesized by emulsion  
25 polymerization using an anionic copolymer of low molecular mass as emulsifier. It is known to a person skilled in the art that the absence of surfactant

during the synthesis and a very fine particle size are preferable in obtaining satisfactory effectiveness during the surface treatment. Patent US 08,434,600 discloses, for example, the emulsion synthesis from  
5 styrene-acrylic acid copolymers used without cosurfactant to give emulsions with a particle size of 65 nm, while Patent FR 9606737 claims the use of dispersions with a size of approximately 55 nm synthesized using styrene-maleic anhydride (SMA)  
10 copolymers.

On the other hand, these anionic emulsions have certain disadvantages. In particular, they show little attachment to cellulose fibres which are slightly anionic, which causes recycling problems in  
15 closed circuits. A high dosage is necessary in order to obtain good sizing properties, because a portion of the dispersion does not remain at the surface and spreads throughout the thickness of the paper sheet. Furthermore, such anionic emulsions are not compatible  
20 with some starches, such as, for example, cationic starches.

Cationic dispersions have therefore been envisaged as sizing agents. Several methods of synthesis are possible. That which proves to be the  
25 most relevant and which the present invention relates to is emulsion polymerization using a cationic copolymer of low mass. Patent DE 2,454,397 claims the

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use of oligomers based mainly on styrene and on dimethylaminoethyl acrylate which are synthesized in an organic solvent. Patent DE 3,401,573 claims the use of styrene, acrylonitrile and dimethylaminoethyl acrylate or methacrylate terpolymers. These two processes have the disadvantage of using an organic solvent which has to be removed before or after the emulsion polymerization. They are therefore neither economical nor ecological. Furthermore, there may be problems of stability of the emulsion at high temperatures typical of sizing baths or at a high shear gradient. Another patent, DE 4,200,715, claims the use of a hydrophobic modified cationic polyamidoamine. This process results in emulsions with a very low solids content and with particle sizes of about 160 nm. These emulsions are therefore neither economical nor effective in the present application.

According to the prior art, it therefore proves to be impossible to use, as sizing agent, cationic emulsions which have a high solids content, which have a fine particle size and which are synthesized without organic solvent or surfactant.

United States Patent US 3,444,151 discloses, however, the synthesis of imide derivatives (II) of copolymers based on maleic anhydride (I) and claims their use in emulsion polymerization for the purpose of latex synthesis. However, this patent claims the use of

compound (II) in a proportion of 2 to 20% by weight with respect to the monomers, which is in fact insufficient for the purpose of obtaining correctly stabilized latices in the absence of conventional  
5 surfactant (the examples taken up in the patent are, moreover, all based on the joint use of conventional surfactant).

The present invention provides a simple process for the synthesis of cationic emulsions and for  
10 the application of these emulsions to paper, which give much better results than the equivalent anionic emulsions.

The present invention is distinguished from the prior art in that it uses cationic emulsions of a  
15 novel type which are intended to be used as sizing agent, which emulsions are obtained in the presence of imide derivatives (II) of copolymers based on maleic anhydride which are used in sufficient proportions to avoid recourse to conventional surfactants. The  
20 emulsions thus synthesized have high hydrophobicity, a fine particle size, a high solids content, weak foaming and good mechanical stability, good stability towards freezing/thawing and good stability at high temperatures. They can be used equally well as surface  
25 sizing agent and as internal sizing agent. In the surface application, they are compatible with a large number of starches. In the internal application, they

make possible immediate sizing without the use of a retention agent.

The invention therefore relates to the application, as sizing agents for papers, of cationic  
5 dispersions resulting from the emulsion polymerization of a mixture of mainly hydrophobic monomers in the presence of an aqueous solution of imide derivatives of copolymers based on maleic anhydride of low molecular mass and in the absence of conventional surfactant.  
10 Emulsion synthesis using these copolymers results in strongly hydrophobic cationic dispersions, with a high solids content and with a low particle size, which confer both very good hydrophobicity on the papers treated and good ink-jet printability.

15 One of the subject-matters of the invention is the aqueous dispersion of hydrophobic polymers which can be used alone or in combination with other agents as sizing agent for paper. It can be obtained according to the process described hereinbelow, which itself  
20 constitutes another subject-matter of the invention.

The process for producing the aqueous dispersion used as sizing agent for papers is carried out by emulsion polymerization starting from an imide derivative (II) of a copolymer based on maleic  
25 anhydride. The synthesis of these derivatives, based on the reaction of a diamine and of a polymer (I) based on maleic anhydride, is disclosed in Patent US 3,444,151.

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Briefly, these imide derivatives are obtained by reaction between a polymer (I) and a primary tertiary diamine, for example dimethylpropylenediamine (DMPA), preferably by a bulk process. The primary amine  
5 functional group will react with the anhydride functional group to form an amic acid and then this ring will reclose to form an imide derivative (II) of the polymer (I). The amine derivatives used in this invention are preferably those of the type I disclosed  
10 in Patent US 3,444,151, that is to say those where a diamine reacts completely with the anhydride functional group with a molar ratio of 1 to 1. The use of copolymers exhibiting residual anhydride or acid functional groups, resulting from a reaction with a  
15 deficiency of amine, is also possible.

The polymer (I) can be a copolymer or a terpolymer composed of maleic anhydride and of hydrophobic monomers chosen from  $\alpha$ -olefins, unsaturated ethylenic aromatics, vinyl ethers or allyl ethers. The  
20 preferred copolymer of the invention is a copolymer of styrene and of maleic anhydride (SMA) with a styrene to maleic anhydride ratio of 1/1 to 6/1, preferably of 2/1 to 4/1. The number-average molecular mass of the emulsifying copolymer is between 500 and 20,000,  
25 preferably between 2000 and 5000. The percentage by mass of this oligomer in the final dry matter is between 10% and 40%, preferably between 20% and 30%.

The polymer (I) will preferably be chosen from copolymers of styrene and of maleic anhydride having acid numbers ranging from 500 to 200 mg KOH/g and sold by the company Elf Atochem under the names of  
5 SMA® 1000, SMA® 2000, SMA® 3000, SMA® EF30, and SMA® EF40 and SMA® EF60.

After imidization, the copolymer is subsequently dissolved in aqueous solution and neutralized with an acid to give a cationic emulsifying  
10 oligomer. The acid used will preferably be a volatile weak acid, such as ethanoic or methanoic acid.

The cationic emulsion is then synthesized, using conventional techniques for emulsion polymerization, in an aqueous solution comprising an  
15 appropriate amount, preferably 30 to 50% with respect to the monomers, of the cationic emulsifier (II) described above and without addition of conventional macromolecular surfactant, in the presence of a conventional radical initiating system and of a mixture  
20 of ethylenically unsaturated monomers, for example composed of styrene and of (meth)acrylic esters.

The radical initiator can be a water-soluble initiator, such as ammonium, potassium or sodium persulphates, optionally used in combination with a  
25 reducing agent of sodium metabisulphite type, or alternatively hydrogen peroxide or a hydroperoxide, such as tert-butyl hydroperoxide, in combination with a

reducing agent, such as ascorbic acid or sodium formaldehydesulphoxylate. This initiator can also be soluble in organic media, such as azo derivatives, for example azobisisobutyronitrile, or organic peroxides.

5           The polymerization temperature is between 30°C and 100°C, preferably between 60°C and 90°C, and will be adjusted to the initiating system used.

          The monomers are chosen in particular so as to obtain the desired glass transition temperature (T<sub>g</sub>)  
10 but also the desired polarity, the desired functionality or the desired degree of cross-linking. This T<sub>g</sub> can be between -70°C and 100°C, preferably between 0°C and 50°C.

          By way of example, the monomers will be  
15 chosen from methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate and more generally alkyl (meth)acrylates of formula:

$$\text{CH}_2=\text{C}(\text{R}_1)\text{COOR}_2$$
, with  $\text{R}_1=\text{H}$  or  $\text{CH}_3$  and  $\text{R}_2$  a group comprising 1 to 22 C,

20           perfluoroalkyl (meth)acrylates of formula:

$$\text{CH}_2=\text{C}(\text{R}_1)\text{COO}-(\text{CH}_2)_n-\text{C}_{n'}\text{F}_{2n'+1}$$
, with  $\text{R}_1=\text{H}$  or  $\text{CH}_3$ ,  
 $n=1-4$  and  $n'=1-14$ ,

          vinyl acetate, styrene, versatic esters, acrylic acid, methacrylic acid, acrylamide, ethylene  
25 glycol dimethacrylate, and the like.

          The cationic dispersions of the invention have a solids content of between 20% and 50%,

preferably between 40% and 50%, and a particle size of between 50 nm and 300 nm with a mean particle size preferably of less than 100 nm. They have very good compatibility with the starches liable to be used in the size press, even at high temperature, whether these are native starches, weakly anionic starches or cationic starches. They have a low viscosity, preferably of less than 100 mPa·s for a solids content of 41%. They have very good stability over time, very good mechanical stability and very good resistance to the freezing/thawing cycle. They confer very good hydrophobicity on the papers treated, at treatment levels far below those of an equivalent anionic emulsion. In particular, they make possible the surface treatment of papers of test liner type intended for board packing, where the papers are required to have very good hydrophobicity. They also make it possible to use, inter alia, a starch and pigments which are cationic during the surface treatment of the paper and to obtain very good ink-jet printability. This is because the particles present in the printing inks are generally anionic and will attach more easily to the surface of the paper if cationic components are present.

Processes for the treatment of paper by external or internal sizing are described in the applicational examples.

### Examples

The following examples illustrate the invention without limiting the scope thereof.

#### 5        **Synthesis examples**

##### Example 1:

##### Synthesis of the cationic surface-active agent

10        This example describes the process for the synthesis of an imide derivative of a styrene-maleic anhydride copolymer denoted by SMA.

15        Dimethylpropylenediamine (DMPA) and then SMA are first of all introduced, at ambient temperature, into an electrically heated two-litre reactor equipped with a stirring device suitable for viscous media. The reaction mixture is then heated to 150°C before starting the stirring and is then brought to 200°C. From this moment on, stationary conditions are maintained for 75 minutes before the imidized SMA is  
20        extruded via the bottom valve of the reactor into a liquid nitrogen bath. The imidized SMA obtained is subsequently milled.

25        For Example S1-1, the reaction mixture comprises 170 g of DMPA and 830 g of an SMA copolymer composed of 79.8% by mass of styrene and 20.2% by mass of maleic anhydride with a number-average molecular

mass of 3000 (commercially available under the name of SMA® EF40 from Elf Atochem S.A.).

A powdered copolymer S1-1 is obtained, the characteristics of which are as follows:

- 5                   Residual DMAPA = 600 ppm  
                   Tg = 112°C  
                   Acid number = 7.5 mg KOH/g.  
                   Examples S1-2, S1-3 and S1-4

10                   The same type of test can be carried out with  
                   other copolymers of styrene and of maleic anhydride  
                   exhibiting other styrene/maleic anhydride ratios, the  
                   nature of the products employed, the amounts used and  
                   the final characteristics of the products obtained  
                   being summarized in the following table:

15

Reference	S1-2	S1-3	S1-4
SMA nature	SMA® 1000	SMA® 2000	SMA® 3000
Amount of SMA (g)	690	760	800
Amount of DMAPA (g)	310	240	200
Acid number (mg KOH/g)	7	2.6	10.6
Level of residual DMAPA (ppm)	600	600	600
Tg (°C)	82	80	91

Example 2:

Dissolution of the cationic surfactant (SUR)

171 g of the SUR S1-1, 644 g of water and 39 g of glacial acetic acid are introduced into a three-necked glass reactor with a capacity of 1 litre equipped with a central stirrer, a condenser, a temperature probe and a device for introducing acetic acid. The combined reactants are heated to 60°C and kept stirring until the oligomer has completely dissolved.

The aqueous solution S2-1 obtained has an S1-1 concentration of approximately 20%. The dissolution of the SUR can optionally be carried out directly in the polymerization reactor as a preliminary stage of Example S3-1.

Example 3:Synthesis of the cationic dispersion

This example describes the synthesis of a cationic dispersion according to the invention.

642 g of aqueous solution S2-1 comprising 20% of oligomer S1-1 are introduced into a jacketed glass reactor with a capacity of 1 litre equipped with a central stirrer, a condenser, a temperature probe and a device for continuously introducing an initiator solution and a mixture or pre-emulsion of monomers, and the reaction mixture is brought to 85°C.

Furthermore, an initiator solution is prepared by dissolving 3 g of ammonium persulphate in

60 g of demineralized water, and a mixture of monomers is prepared composed of 138 g of styrene and 162 g of butyl acrylate.

When the reaction mixture is at 85°C, the  
5 initiator solution and the mixture of monomers are fed in over a period of 2 hours, with stirring and while maintaining the temperature at 85°C.

The reaction mixture is then kept stirring for an additional two hours at 85°C, then cooled to  
10 ambient temperature, filtered through a 100 µm cloth and drained to result in the S3-1 dispersion, which exhibits the following characteristics.

Solids content = 41%

Viscosity is 35 mPa·s, measured using a  
15 Brookfield device at 25°C according to the Standard

pH = 4

Mean diameter of the particles = 95 nm

Tg = 25°C

Comparative Example 1

20 A sizing agent is synthesized in the same way as that disclosed in Example 1 of Patent FR 9606737, to give an anionic emulsion S4 stabilized by a styrene-maleic anhydride copolymer neutralized with ammonia, composed of 74.3% by mass of styrene and 25.7% by mass  
25 of maleic anhydride. This emulsion is therefore the anionic equivalent of the emulsion S3-1.



This emulsion S4 exhibits the following characteristics:

Solids content = 23.5%

Brookfield viscosity at 25°C = 20 mPa·s

5 pH = 8.85

Mean diameter of the particles = 55 nm

Tg = 25°C

**Applicational examples**

Three papers are surface treated using a  
10 laboratory-scale size press.

The first two, of printing and writing type, have a grammage of 80 g/m<sup>2</sup> and are sized with alkyl ketene dimer (Aquapel® 315 from Hercules, hereinafter AKD) at a level of 0.2% or 0.6% with respect to the  
15 weight of the paper.

Another paper of the test liner type intended to be used for the packing board application has a grammage of 130 g/m<sup>2</sup> and was not subjected to any internal sizing.

20 The following two tests were carried out in order to measure the hydrophobicity and the resistance to penetration by aqueous solutions of the papers treated:

Cobb test: this test is well known to a  
25 person skilled in the art and is described in NF Standard EN 20535-ISO 535. The amount of water absorbed after a given time is given in g/m<sup>2</sup>. In this

instance, the Cobb test is carried out with a contact time of 60 seconds (Cobb<sub>60</sub>) or of 30 minutes (Cobb<sub>1800</sub>).

HST test: this test is carried out according to Tappi Test Methods T Standard 530 OM-96. The papers  
5 to be tested have a size of 6 × 6 cm and are subjected, on one face, to a green ink (prepared with 1.25% of Naphthol Green B dye, 1% of formic acid and the remaining percentage of demineralized water). The penetration time of the aqueous ink is determined by  
10 reflection of a light source on the opposite face when the percentage of reflection reaches 80%.

#### Example A1

This example shows the advantage of the sizing agents according to the invention in the surface  
15 treatment of printing and writing papers with regard to their resistance to water and to penetration of the ink. An acceptable printing and writing paper must have a Cobb<sub>60</sub> of less than 30 and an HST of greater than 100.

The paper treated with 0.2% of AKD is surface  
20 sized with an aqueous solution comprising:

3% by weight of weakly anionic starch Amylis®  
100 P (Roquette)

0.25% and 0.5% by weight of active material  
of the emulsions S3-1 and S4

25 The solution being brought to 100% by addition of the necessary complementary demineralized water.

The following results clearly show the superiority of the application according to the invention at a low treatment amount compared with the application using an anionic sizing agent:

5

Products	Starch alone	S3-1 0.25%	S3-1 0.5%	S4 0.25%	S4 0.5%
Cobb <sub>60</sub> (g/m <sup>2</sup> )	> 100	27.5	22.5	71	23
HST (s)	0	127	197	24	190

#### Example A2

This example shows the advantage of the sizing agents according to the invention in the surface treatment of printing and writing papers using a cationic starch. The latter introduces significant advantages with regard to the printability properties.

The papers treated with 0.2% and 0.6% of AKD are surface sized with a solution comprising:

15                   3% by weight of cationic starch Catosize® 240  
(National Starch)

0.5% by weight of active material of the emulsions S3-1 and S4

The solution being brought to 100% by  
20 addition of the necessary complementary demineralized water.

The following results, in comparison with those of Example A1, clearly show the compatibility of the dispersion according to the invention with any type of starch. Whereas the properties of the emulsion S3-1 are reinforced in the presence of a cationic starch, those of the emulsion S4 decline and are even inferior to those of the starch alone for the paper with 0.6% of AKD, due to an incompatibility in the sizing slip.

10 Paper with 0.2% of AKD

Products	Starch alone	S3-1	S4
Cobb <sub>60</sub> (g/m <sup>2</sup> )	100	20.7	65
HST (s)	0	300	8

Paper with 0.6% of AKD

Products	Starch alone	S3-1	S4
Cobb <sub>60</sub> (g/m <sup>2</sup> )	52.5	19.5	59.5
HST (s)	9	120	7

15

#### Example A3

This example shows the advantage of the sizing agents according to the invention in the surface treatment of packing board papers, with regard to their resistance to water. For these papers, very good

20

resistance to water is required over long periods of time. An acceptable paper of test liner type intended for packing board must have a Cobb<sub>1800</sub> equal to or less than 120.

- 5                   The paper of test liner type described above is surface sized with a solution comprising:

8% by weight of weakly anionic starch Amylis®  
100 P (Roquette)

- 0.7% and 1.2% by weight of active material of  
10 the emulsions S3-1 and S4

The solution being brought to 100% by addition of the necessary complementary demineralized water.

- The following results demonstrate the  
15 possibility of treating, with reasonable amounts of sizing agent according to the invention, papers of test liner type which have not been subjected to any internal sizing.

Products	Starch alone	S3-1 0.7%	S3-1 1.2%	S4 0.7%	S4 1.2%
Cobb <sub>60</sub> (g/m <sup>2</sup> )	200	30	20	61	28
Cobb <sub>1800</sub> (g/m <sup>2</sup> )	250	150	105	165	150

Example A4

This example describes the use of the cationic dispersion of the invention as internal sizing agent.

5           The paper is obtained according to the process which consists in preparing handsheets on a Franck device starting from a pulp beaten to a certain Schopper-Riegler degree of drainability (see NF Standard Q 50003). The sizing agent is added to the  
10 fibrous suspension composed of 5 g/l of fibres in water. Stirring is continued for 3 minutes. The handsheet is prepared at a mean grammage of 65 g/m<sup>2</sup>, after draining, dewatering and drying for 5 minutes at 95°C. The pulp used in this instance is composed of 50%  
15 short fibres and 50% long fibres and has a Schopper-Riegler degree of 25.

1% of sizing agent with respect to the dry fibrous matter is added. The sizing agents used are emulsions S3-1 and S4, as well as AKD (Aquapel® 315  
20 from Hercules). The handsheets treated with AKD are subjected to accelerated maturing in an oven for 10 minutes at 110°C.

Sizing agent	None	AKD	S3-1	S4
Cobb <sub>60</sub>	> 100	42	24	> 100

As is seen in the light of these results, the emulsion S3-1 gives entirely satisfactory sizing results without a retention agent, whereas the performance is mediocre with AKD used alone.

- 5 Furthermore, no maturing stage is necessary. The anionic emulsion does not give any result because it is not attached to the fibres.